THE EFFECT OF MINERAL SPECIES ON OIL SHALE CHAR COMBUSTION

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INTRODUCTION

In order to increase the energy efficiency of above-ground oil shale processes, the carbonaceous residue ("char") remaining on retorted oil shale ("spent" shale) will either be combusted (1,2) or gasified (3). Although there is no great difficulty in combusting the char, it is important that combustion be carried out in a controlled fashion. Failure to do so can result in high temperatures (>900°K) and the decomposition of mineral carbonates. These decomposition reactions are not only endothermic (4) but some of the products have the potential to cause environmental disposal problems (5).

Control of oil shale char combustion is more easily managed if there is a knowledge of how the rate of combustion depends on O_2 concentration and temperature. This motivation led to an earlier study (6) of the combustion kinetics of spent shale from the Parachute Creek Member in western Colorado. That study provided evidence that one or more of the mineral species present in the shale acted as an oxidation catalyst. Consequently it was decided to follow up on that investigation by examining the combustion activity of other oil shales; specifically those with differing elemental and/or mineral compositions.

Six oil shale samples were selected for evaluation and comparison: one from the Parachute Creek Member (PCM), one from a deep core sample in the C-a tract (C-a), two from the saline zone in western Colorado (S-A and S-B), one from the Geokinetics site in eastern Utah (GEOK) and one sample of Antrim shale from Michigan (ANT).

EXPERIMENTAL

Figure 1 shows a schematic sketch of the experimental equipment. Approximately 1.5 g of spent shale (particle size ~100μ) was placed in a 400 mesh stainless steel basket which was suspended from a recording electro-balance to provide continuous gravimetric readings as combustion proceeded. The reactor vessel was constructed of 310 stainless steel and placed in a 4" furnace capable of reaching temperatures as high as 1200°K. Any one or a mixture of gases can be metered to the reactor via a 1/4" sparge tube and provisions are made to sample the exit gases with on-line gas chromatography. Tracer tests indicate that the design of the sparge system effectively creates an ideal back-mix state. Temperatures are monitored and controlled by means of two 1.6 mm shielded chromel-alumel thermocouples; one placed approximately 2 cm above the basket and the other so that it barely touches the shale sample. The latter was used to monitor temperature excursions during initial combustion but never exceeded 10 K and, then, only for 1-2 minutes.

All of the shale samples were retorted in master batches and under identical conditions in a 2.5 cm diameter fixed bed retort. A nitrogen sweep gas at 100 cc/min was employed and the temperature was elevated at a rate of 5 K/min to a maximum temperature of 785°K at which point it was held for 1 hour. Table I shows the quantity of oil collected during retorting, the percentage of organic carbon on the spent shale and the percentage of some of the more important elements (obtained by X-ray fluorescence). Although there is a wide variation in the oil yields, we have previously shown (7) there to be no effect on the combustion activity of spent shale. However, it is interesting to note that the GEOK sample had twice the organic carbon content of the PCM sample even though the two had similar oil yields.

Combustion tests were carried out by heating the sample to the desired temperature in a helium atmosphere and then exposing it to a pre-selected O_2 concentration. In some cases the samples were first subjected to high temperatures (800-1050°K) in either a helium or CO_2 atmosphere in order to effect changes in the mineral compositions and then cooled to the desired combustion temperature. Combustion activities were evaluated for O_2 pressures between 5 and 20 kPa and at temperatures between 700 and 825°K.

TABLE I

COMPOSITION OF SPENT SHALE SAMPLES

Sample	GPT[a]	C[b]	Ca	Mg	Fe	Al	Na	K	Si
PCM	50	5.1	10.2	3.4	2.8	5.0	2.6	1.7	18.8
C-a	25	3.5	12.3	3.5	2.5	4.3	2.0	1.7	16.2
GEOK	44	11.9	15.2	4.3	3.1	4.8	2.3	2.0	19.6
S-A	30	3.8	8.4	3.6	3.1	6.3	2.8	2.1	22.3
S-B	40	3.9	1.0	1.0	5.6	10.9	0.4	1.7	30.2
ANT	11	7.0	0.7	1.2	5.4	8.3	0.4	3.4	31.0

Wt% Spent Shale (header spanning Ca–Si columns)

a. Gallons per ton
b. Organic carbon

RESULTS

As in our earlier work (6) the combustion reaction rate was found to be first order with respect to both O_2 and char content. Table II lists the apparent rate constants in terms of the pre-exponential factor and the activation energy for all six samples as well as comparative values at 700°K. The S-A sample had the highest activity and has high concentrations of the minerals dawsonite and nahcolite. Although these minerals will have decomposed during retorting, the decomposition products (Na_2CO_3, Al_2O_3) are present and, as we will show, there is strong evidence to indicate that they act as catalysts. In view of this, it is also tempting to conclude that the low apparent activation energy is also due to a catalytic mechanism. However, because of the high reaction rate and the limitations on the maximum gas flow rate in the TGA system, it is possible that gas-solid mass transport has influenced these measurements. It is interesting, but probably coincidental, that the S-B shale had the lowest activity. This sample is similar to S-A except that it is low in dawsonite and nahcolite. Finally, it should be pointed out that the pre-exponential factor listed in Table II for the PCM sample, differs from the value we reported earlier (6). By virtue of our measurements of the actual shale temperature, we have discovered that the measured temperatures in the earlier study were in error. The values listed in Table II are now consistent with the reported measurements of Sohn and Kim (8).

TABLE II

KINETIC PARAMETERS

$$k = k_o EXP\left[\frac{-E}{RT}\right] \quad (kPa\text{-}min)^{-1}$$

Sample	ko x 10^{-5}	E[a]	k (700 K)
PCM	2.45	97.07	.0140
C-a	8760.	142.3	.0212
GEOK	11.51	91.21	.0236
S-A	.002	49.79	.0385
S-B	.480	93.72	.0049
ANT	5.42	104.8	.0082

a. KJ/mol

One of the experiments which we initially conducted on the PCM sample was to thermally decompose the carbonate minerals (dolomite and calcite) to their oxides at 900°K

$$Ca\,Mg\,(CO_3)_2 \longrightarrow CaO + MgO + 2\,CO_2 \qquad \text{1)}$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad \text{2)}$$
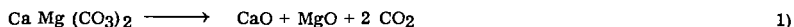
When the temperature was lowered to 700°K and the sample exposed to O_2, the observed combustion rate was ten times higher than when the carbonates were left intact. By process of elimination, the increased activity was attributed to the presence of CaO. In order to further investigate this phenomena, the same experiment was carried out with the C-a and ANT sample. The C-a sample was chosen due to the fact that its free calcite was only 2% compared to 10% for the PCM sample. On the other hand, the ANT sample had a very low Ca content.
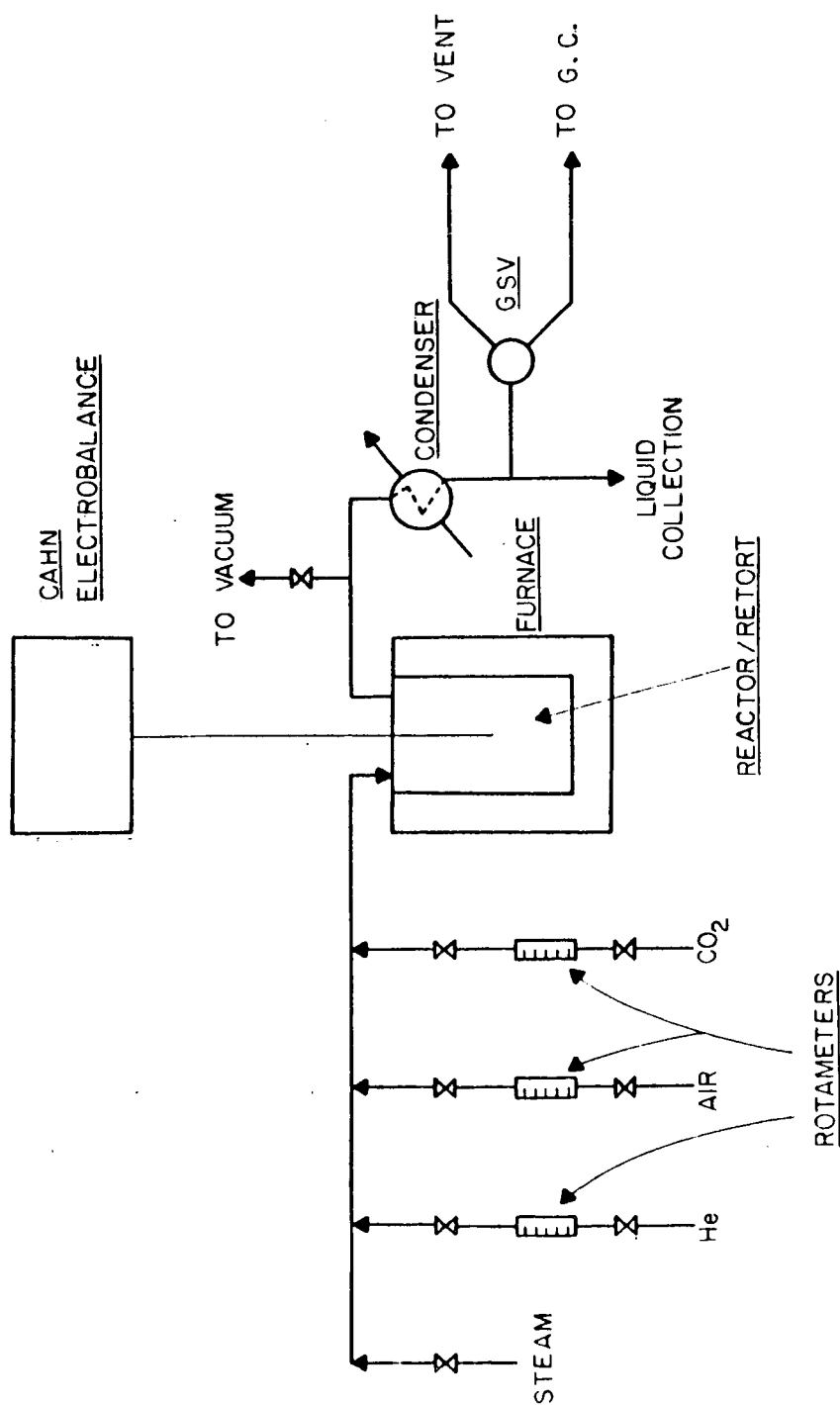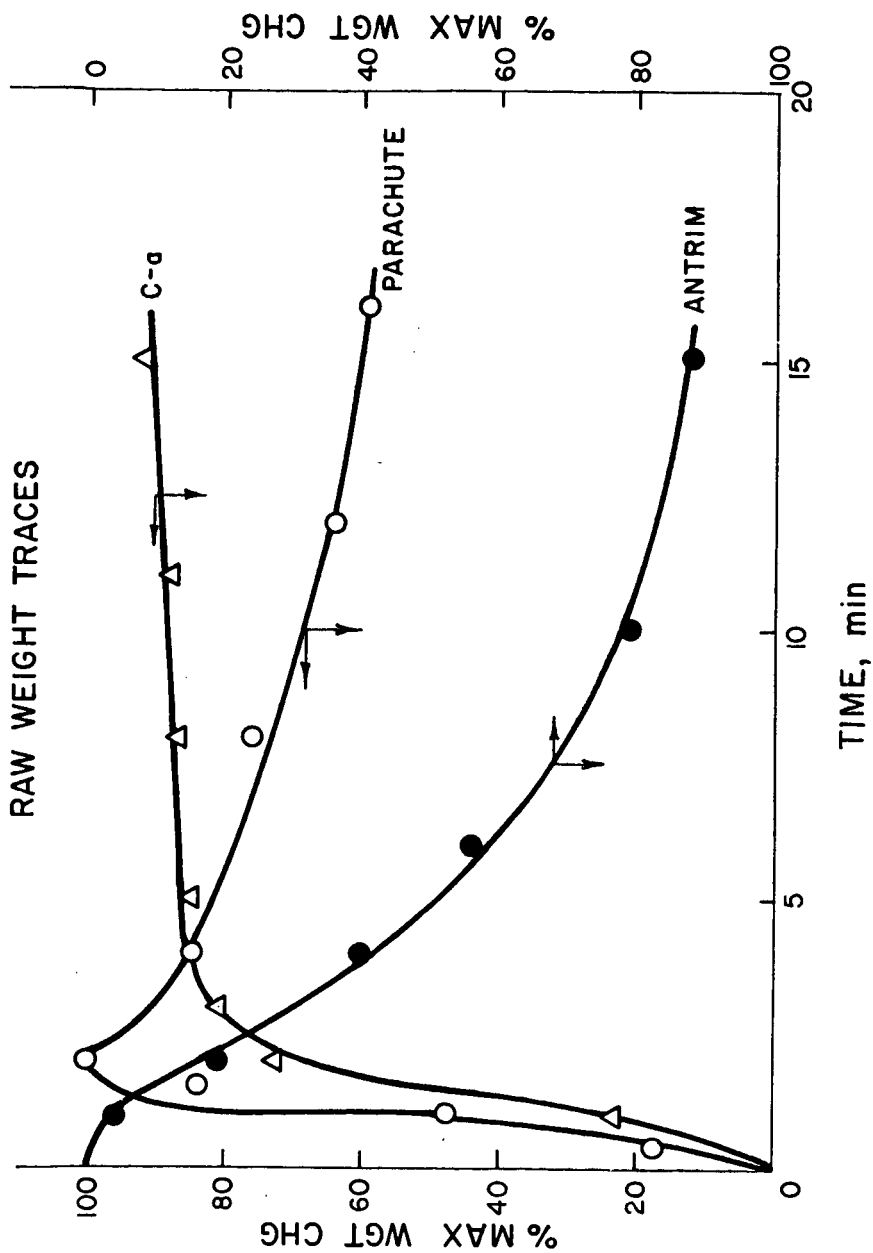
FIGURE 1: EXPERIMENTAL SCHEMATIC.

238

Figure 2

RAW WEIGHT TRACES

Figure 3

EFFECT OF THE Na ON CHAR COMBUSTION (700 K, P_{O_2}=.10 AtM)

O UNWASHED
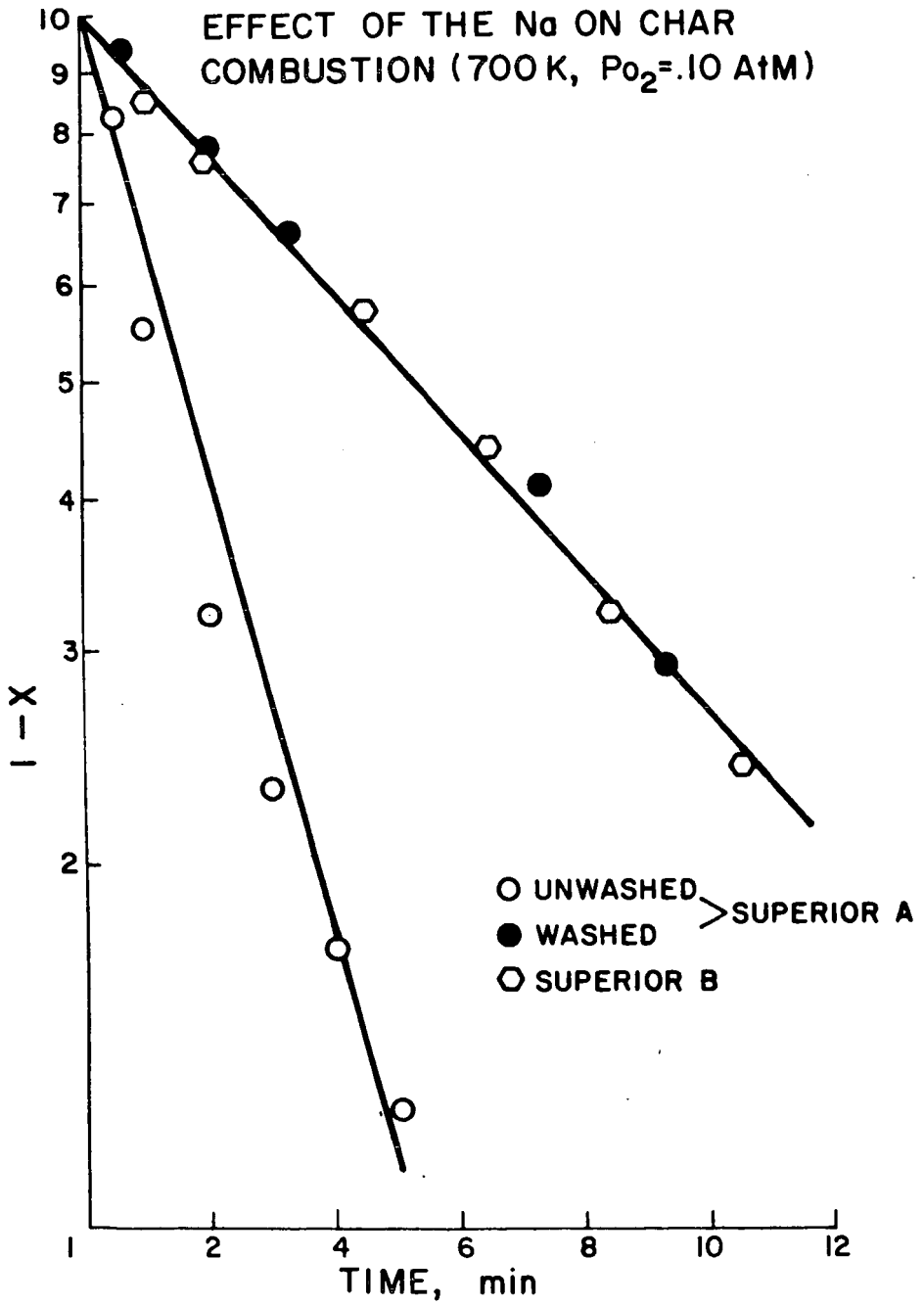● WASHED   >SUPERIOR A

⬡ SUPERIOR B

Figure 2 shows the comparative responses of the raw gravimetric readings when the decomposed samples were exposed to 10% O_2 at time = C. Similar behavior is observed for the C-a and PCM samples; that is, the raw weight increases due to the recarbonation of CaO.

$$C + O_2 \longrightarrow CO_2 \qquad\qquad 3)$$

$$CaO + CO_2 \longrightarrow CaCO_3 \qquad\qquad 4)$$

Since the combustion rate is at least as fast as the recarbonation rate, the data in Figure 2 correspond to a combustion rate increase of about an order of magnitude in both samples. This also leads to the conclusion that the source of CaO does not appear to be important since most of it is produced from ankeritic dolomite in the C-a sample and over 30% from free calcite in the PCM sample. It is interesting to note that the ANT sample, which has minimal Ca, does not experience a weight gain during combustion. In fact, the combustion rate is identical to that observed for ANT samples which had not been thermally pretreated. Since the latter is also high in iron compounds, these results tend to support the hypothesis of CaO as a combustion catalyst.

Additional experiments were also run in order to examine the effects of mineral species. Figure 3 shows first order plots for two S-A and one S-B sample. As pointed out earlier, the S-A and S-B samples are similar except for high concentrations of nahcolite and dawsonite in the former and this sample had the highest combustion activity (Table II). The effect of the sodium contained in these minerals was examined by water leaching the S-A sample prior to combustion. As can be seen, this reduces the combustion activity so that it becomes identical to the S-B activity. These results are not too surprising since it is well known that the Group I-a and, to a lesser extent, the Group II-a elements are good gasification catalysts (9).

At temperatures between 925-1100°K, western shales will form Ca-Mg silicates if calcite decomposition can be prevented. In order to investigate the consequences of having silicates present during combustion, both the PCM and C-a samples were raised to 1100°K in a 20% CO – 80% CO_2 atmosphere and held at that temperature until silication was completed. The CO_2 atmosphere prevented Reaction 2 from taking place and the CO was used to inhibit the CO_2 – char reaction (10). The samples were then cooled and subjected to combustion conditions. Although both samples had over 50% of their char remaining, it was impossible to combust either at the conditions used in this study. Apparently the silication process acts to encapsulate the char and render it inactive to normal combustion conditions.

CONCLUSIONS

On the basis of the studies conducted here, it is readily apparent that the presence of minerals can drastically alter the reactivity of the residual char on spent oil shale. More detailed quantitative studies are necessary in order to be able to assess their importance under typical oil shale processing conditions and will be the subject of future manuscripts from this laboratory.

ACKNOWLEDGMENT

LITERATURE CITED

(1)   Hall, R. N., paper presented at National AIChE Meeting, Anaheim, CA, June 8, (1982).
(2)   Griswold, C., and Duir, J. H., paper presented at National AIChE Meeting, Anaheim, CA, June 8 (1982).
(3)   "Union Oil's SGR Process", Oil and Gas J., June 17, p. 26 (1974).
(4)   Campbell, J. H., Lawrence Livermore Lab., Rept. No. UCRL-52089 part 2, March (1978).
(5)   Mavis, J. D., and Rosain, R. M., paper presented at National AIChE Meeting, Detroit, MI, August 16 (1981).
(6)   Soni, Y., and Thomson, W. J., I and EC Proc. Des. and Dev., $\underline{18}$, 661 (1979).
(7)   Soni, Y., and Thomson, W. J., Proceedings of 11th Oil Shale Symp., p. 364, April (1978).
(8)   Sohn, H. Y., and Kim, S. K., I and EC Proc. Des. and Dev., $\underline{19}$, p. 550 (1980).
(9)   Wen, W. Y., Catal. Rev. - Sic. Eng., $\underline{22}$, 1 (1980).
(10)   Thomson, W. J., Gerber, M. A., Hatter, M. A., and Oakes, D. G., "Oil Shale Tar Sands and Related Materials", ACS Symp. Ser. 163, p. 117 (1982).